cyclopropyl carbinyl carbocation rearrangement (Sakkers, Vankan, Klunder & Zwanenburg, 1979). Such a rearrangement reaction is also observed when (1) is treated with HCl or HBr in methanol, resulting in (3). The initially formed cyclopropyl cation, in this case, reacts rapidly with the bromide anion. In the absence of such a strong nucleophile, further bond reorganization leads to the tetracyclo[4.4.0.$0^{2,8}$.$0^{4,7}$]dec-9-en-5-one system (2). (4) has the molecular structure anticipated for (1) and shows the *endo* configuration of the dinitrophenyl ester function. Bond distances and angles are all in the range expected for these strained structures and no intermolecular distances significantly shorter than expected from van der Waals contacts are observed.

In (4), the distance between C(8) and the olefinic carbon atoms C(16) and C(17) is 2·90 Å. The molecular-mechanics calculation on (1) gives values of 2·70 and 3·34 Å respectively for the distance between the carbonyl carbon and the olefinic bond and the carbonyl oxygen atom and the olefinic bond. These distances indicate an interaction between the two double bonds in compound (1) as suggested by its UV spectrum.

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Dipyridinium Oxalate–Oxalic Acid

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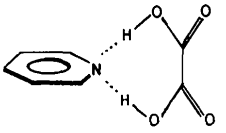
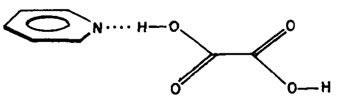
Abstract. $2C_5H_6N^+.C_2O_4^{2-}.C_2H_2O_4$, $M_r = 338\cdot3$, triclinic, $P\bar{1}$, $a = 3\cdot999\,(2)$, $b = 8\cdot439\,(4)$, $c = 11\cdot319\,(3)$ Å, $\alpha = 77\cdot96\,(3)$, $\beta = 88\cdot64\,(2)$, $\gamma = 82\cdot69\,(3)°$, $V = 370\cdot5\,(4)$ Å^3, $Z = 1$, $D_x = 1\cdot516$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 1\cdot18$ cm^{-1}, $F(000) = 176$, $T = 301$ K, $R = 0\cdot041$ for 1390 observations (of 2155 unique data). The title structure consists of two pyridinium ions hydrogen bonded to one oxalate ion, which lies on a center of symmetry. An additional centrosymmetric oxalic acid molecule forms hydrogen bonds with the oxalate moiety to give linear chains along the *c* axis.

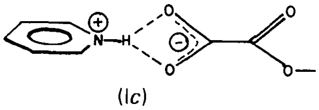
Introduction. A 1:1 adduct between pyridine and oxalic acid was first reported in a solubility study (Grigorowsky & Kimen, 1945). Considering the reduced acidity of the second proton of oxalic acid, an equimolar mixture of pyridine and oxalic acid would be expected to give a pyridinium hydrogen oxalate species (pyridinium = pK_a 5·25; oxalic acid = pK_a 1·23, 4·19). Three possible interactions of a 1:1 adduct, as depicted in the scheme below, are: a μ-bonded pyridine to both acidic protons (I*a*) or pyridine interacting with one acidic proton in either of two fashions (I*b* or I*c*). In search of further examples of a pyridine μ-bonding to two atoms (I*a*) (Newkome, Lee & Fronczek, 1985), structure determination of the pyridine–oxalic acid adduct was undertaken.



(I*a*)



(I*b*)



(I*c*)

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Experimental. Equimolar mixture of pyridine and oxalic acid dihydrate in MeOH gave title compound as colorless crystals: m.p. 426–428 K; ^{1}H NMR (CD$_3$OD) δ 7·72–7·89 (*m*, 3-pyH, 2H), 8·30 (*tt*, 4-pyH, $J_{4,3} = 7{\cdot}7$, $J_{4,2} = 1{\cdot}7$ Hz, 1H), 8·76 (*dd*, 2-pyH, $J_{2,3} = 4{\cdot}7$ Hz, 2H). Colorless tabular crystal of dimensions 0·16 × 0·42 × 0·45 mm, capillary mounted. Space-group determination by successful refinement of centrosymmetric model. Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo $K\alpha$ radiation. Cell dimensions from setting angles of 25 reflections, $24 < 2\theta < 30°$. Data collection by ω–2θ scans designed for $I = 50\sigma(I)$. Scan rates varied 0·53–5·0° min^{-1}. Reflections having $1 < \theta < 30°$, $0 \leq h \leq 5$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$ measured, corrected for background, Lorentz, polarization effects. Max. $(\sin\theta)/\lambda = 0{\cdot}70$ Å^{-1}. Three standard reflections ±2·5% random variation. Absorption insignificant. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) by phasing in $P1$ from fragments recognized in E maps in $P\bar{1}$. Refinement by full-matrix least squares (based on F) using data for which $I > 3\sigma(I)$ (765 unobserved reflections), $w = [\sigma^2(F) + 0{\cdot}02F^2]^{-1}$, with Enraf–Nonius *SDP* (Frenz & Okaya, 1980). Non-H atoms anisotropic; H atoms located by ΔF and refined isotropically. Final $R = 0{\cdot}041$, $wR = 0{\cdot}057$, $S = 1{\cdot}993$ for 138 variables, largest residual densities 0·33 and 0·36 e Å^{-3} on oxalic acid and oxalate centers, 0·18 e Å^{-3} otherwise, extinction coefficient 3·3 (7) × 10^{-6}, max. shift in final cycle 0·01σ. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer: PDP11/34. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.*

Discussion. Fig. 1 illustrates that the structure contains pyridinium ions, oxalate ions and oxalic acid molecules. Fig. 2 illustrates that the oxalate and oxalic acid molecules are hydrogen bonded in alternating fashion, forming linear chains along the c axis. Each oxalate moiety along the chain *forms two hydrogen bonds to pyridinium cations.* A structure containing both oxalic acid molecules and oxalate ions has been reported (Mutin, Watelle & Dusausoy, 1979). All of the heavy atoms of the pyridinium ion lie within 0·001 (2) Å of a common plane, and the acidic proton bonded to it lies within 0·01 (2) Å of that plane. This pyridinium cation donates a hydrogen bond to O(4) of the oxalate anion, with N···O distance 2·716 (1) Å. Theoretical calculations for the pyridine–HF dimer indicate that the favored geometry for the angle $\mathrm{F\hat{H}N}$ is 180°, *i.e.* a linear hydrogen bond (Del Bene, 1975). However, in this case, the corresponding angle ($\mathrm{O\hat{H}N}$) is only 152 (2)°. Of probable importance in causing this nonlinearity is the somewhat longer contact between pyridinium N and O(3′) of the same oxalate anion. Indeed, the contact between the pyridinium and oxalate ions may best be thought of as an asymmetrically bifurcated hydrogen bond (Thomas, 1977). The N··· O(3′) distance is 2·923 (1) Å, and the N—H···O(3′)

Table 1. *Coordinates and isotropic thermal parameters* (Å^2)

	x	y	z	B or B_{eq}*
O(1)	0·9661 (3)	−0·0642 (1)	0·15585 (7)	3·95 (2)
O(2)	1·1557 (4)	0·1568 (1)	0·04921 (9)	5·81 (3)
O(3)	0·0789 (3)	1·0372 (1)	0·34501 (7)	3·74 (2)
O(4)	−0·0785 (3)	0·8162 (1)	0·46578 (9)	4·56 (2)
N	0·3562 (3)	0·3450 (2)	0·3301 (1)	4·10 (3)
C(1)	1·0413 (4)	0·0313 (1)	0·0569 (1)	2·90 (3)
C(2)	−0·0019 (4)	0·9560 (2)	0·4459 (1)	2·87 (2)
C(3)	0·4987 (5)	0·3198 (2)	0·2289 (2)	4·27 (3)
C(4)	0·6387 (5)	0·4427 (2)	0·1540 (1)	4·51 (4)
C(5)	0·6269 (5)	0·5910 (2)	0·1863 (2)	4·59 (4)
C(6)	0·4785 (5)	0·6133 (2)	0·2917 (2)	4·68 (4)
C(7)	0·3424 (5)	0·4880 (2)	0·3633 (1)	4·43 (4)
H(10)	1·020 (5)	−0·021 (2)	0·234 (2)	7·5 (6)
H(1N)	0·260 (6)	0·266 (3)	0·384 (2)	7·4 (5)
H(3)	0·488 (5)	0·218 (2)	0·212 (2)	6·3 (5)
H(4)	0·731 (5)	0·421 (2)	0·084 (2)	7·2 (6)
H(5)	0·717 (5)	0·674 (2)	0·133 (2)	6·1 (5)
H(6)	0·472 (5)	0·709 (2)	0·319 (2)	7·3 (6)
H(7)	0·252 (6)	0·488 (3)	0·442 (2)	8·6 (6)

* $B_{eq} = \frac{1}{3}\sum B_{ij}$.

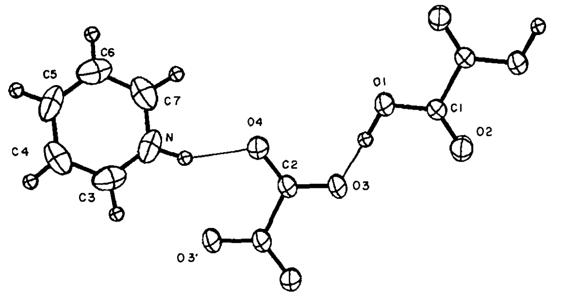

Fig. 1. Numbering scheme and thermal ellipsoids drawn at the 50% probability level.

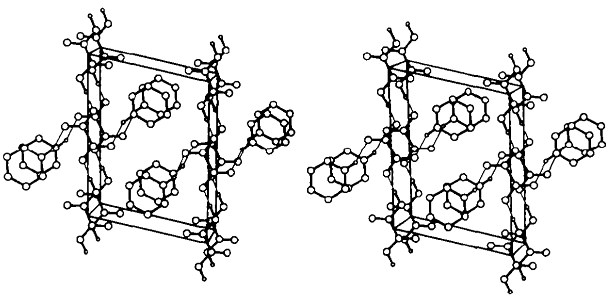

Fig. 2. Stereoscopic representation of the unit cell, viewed slightly oblique to the a axis, with c vertical.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42351 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°)

N–C(3)	1·312 (2)	O(4)–C(2)	1·230 (1)
N–C(7)	1·331 (2)	C(1)–C(1′)	1·548 (2)
N–H(1N)	0·92 (2)	C(2)–C(2′)	1·560 (2)
O(1)–C(1)	1·289 (1)	C(3)–C(4)	1·366 (2)
O(1)–H(10)	1·06 (2)	C(4)–C(5)	1·370 (2)
O(2)–C(1)	1·192 (1)	C(5)–C(6)	1·357 (2)
O(3)–C(2)	1·261 (1)	C(6)–C(7)	1·356 (2)

C–H range: 0·91–0·95 Å

C(3)–N–C(7)	122·1 (1)	O(4)–C(2)–C(2′)	118·4 (1)
C(1)–O(1)–H(10)	112·9 (9)	N–C(3)–C(4)	119·9 (1)
O(1)–C(1)–O(2)	125·9 (1)	C(3)–C(4)–C(5)	119·0 (1)
O(1)–C(1)–C(1′)	112·7 (1)	C(4)–C(5)–C(6)	119·8 (1)
O(2)–C(1)–C(1′)	121·4 (1)	C(5)–C(6)–C(7)	119·2 (1)
O(3)–C(2)–O(4)	126·2 (1)	N–C(7)–C(6)	120·0 (1)
O(3)–C(2)–C(2′)	115·5 (1)		

angle is 127°. The oxalate and oxalic acid moieties are each planar [maximum deviations 0·003 (1) and 0·007 (2) Å, respectively] and the dihedral angle between these planes is 13·0°. The oxalic acid molecule donates a strong linear hydrogen bond to the oxalate ion O(1)–H···O(3) with O···O distance 2·535 (1) Å and O–H–O angle 177·3 (14)°. The difference in hydrogen-bond strength of the two independent oxalate oxygen atoms apparently affects their bonds to carbon, as C(2)–O(3) [1·261 (1) Å] is substantially longer than C(2)–O(4) [1·230 (1) Å].

Bond lengths and angles are given in Table 2. The C(2)–O(3) and C(2)–O(4) distances in the oxalate moiety [1·261 (1) and 1·230 (1) Å, respectively] do not correlate well with the ranges normally found in potassium oxalates [1·2473 (17)–1·2595 (16) Å] (Hodgson & Ibers, 1969; Sequeira, Srikanta & Chidambaram, 1970) nor with oxalates of other nitrogen bases [1·255 (2)–1·261 (1) Å] (Pedersen, 1972; Adams & Pritchard, 1976). However, the similarity to the carboxylate in hydrogen oxalates of nitrogen bases is interesting [1·226 (2)–1·260 (2) Å] (Kuppers, 1973; Currie, Speakman & Curry, 1967; Thomas, 1977; Vijayalakshmi & Srinivasan, 1983). The C–OH bond in the oxalic acid [C(1)–O(1), 1·289 (1) Å] is similar to that in oxalic acid dihydrate [1·291 (5) Å] but the C(1)–O(2) bond length of 1·192 (1) Å is exceedingly short compared to other oxalic acid species [1·204 (2)–1·223 (1) Å] (Sabine, Cox & Craven, 1969; Stevens & Coppens, 1980; Currie, Speakman & Curry, 1967).

Interestingly, and contrary to the $\mathrm{p}K_a$-based conclusions, *one oxalic acid donates two protons to pyridine bases rather than two oxalic acids giving up one proton each!* Bond distances within the pyridinium cation are short by comparison to expected aromatic C–C (1·394 Å) and C–N (1·340 Å) distances. Such shortening is generally observed in crystal structures containing pyridinium. However, most suffer from disorder (Hartl, 1975; Copeland, Conner & Meyers, 1966; Adams & Strähle, 1982; Truter & Vickery, 1972; Tucker & Kroon, 1973) or high thermal motion (DeHaven & Jacobson, 1976; Skarzynski, Stepien, Cygler & Grabowski, 1978; Caputo, Willett & Morosin, 1978; Serewicz, Robertson & Meyers, 1965), and exhibit shortened bond distances. Even a cryogenic (190 K) determination of a pyridinium salt $[\mathrm{C_5H_6N}][(\mathrm{CO})_5\mathrm{CrAsCl_2Cr}(\mathrm{CO})_5]$ (von Seyerl, Sigwarth & Huttner, 1981) exhibited shortening of bonds *versus* expected values. The N atom in that determination is almost certainly misidentified, but taking account of that error yields average C–N (1·31 Å) and C–C (1·37 Å) distances that are close to our values.

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